The paradigm of concretization

Kuipers, Theo A.F.

Published in:
EPRINTS-BOOK-TITLE

Publication date:
1985

Theo A.F. Kuipers/Groningen

THE PARADIGM OF CONCRETIZATION: THE LAW OF VAN DER WAALS*

On many occasions Leszek Nowak (e.g. (1976), p. 164) and others have referred to the transition from the ideal gas law to the law of van der Waals as a paradigm of *concretization*. In this context concretization is primarily understood as a formal relation between two laws, i.e. the one is a limit-case of the other.

As is well-known, the ideal gas law can be explained (derived) on the basis of the kinetic theory of gases. Given the formal concretization relation between the two, it is reasonable to expect, and frequently claimed, that the explanatory argument leading to the ideal gas law can be corrected (concretized) in such a way that we obtain an explanation (derivation) of the law of van der Waals.

We may formulate the general claim that, given a law and a concretization of it, and given a (theoretical) explanation of the former, the explanation of the latter can be described as a *concretization of the explanation* of the former. In this paper we will investigate this claim for the (kinetic) explanation of the law of van der Waals.

It will turn out that the standard account seems a perfect illustration of this general claim only as long as wall-attraction is neglected in the argument, but that this account is essentially defective as soon as it takes wall-attraction into cosideration. Hence, it is no illustration of the general claim at all. Fortunately, it is possible to give a sophisticated, non-defective account illustrating the general claim.

On the phenomenological level (*F*-level) the two laws are, for one mole of gas, as follows:

$$(1) \qquad PV = RT \quad \text{or} \quad P = \frac{RT}{V} \qquad \text{(ideal gas law)}$$

$$(2) \qquad \left(P + \frac{a}{V^2}\right)(V-b) = RT \quad \text{or} \quad P = \frac{V}{V-b}\left(\frac{RT}{V}\right) - \frac{a}{V^2}$$

(van der Waals law)

where P indicates pressure, V volume, T absolute temperature, and R the universal gas constant; a and b are individual gas constants, which are, on

the kinetic level (K-level), related respectively to the mutual attraction and the volume of the molecules.

Using Nowak's general schematization (but inverting his numbering device) we get the following reconstruction of the transition from (1) to (2), assuming P to be the magnitude of interest:

level 1 principal factors $V, T, (R)$

level 2 secondary factors a, b

with the respective "theorems"[1]:

(1*) if $a = 0$ and $b = 0$ then $P = f_1(V, T) = \dfrac{RT}{V}$

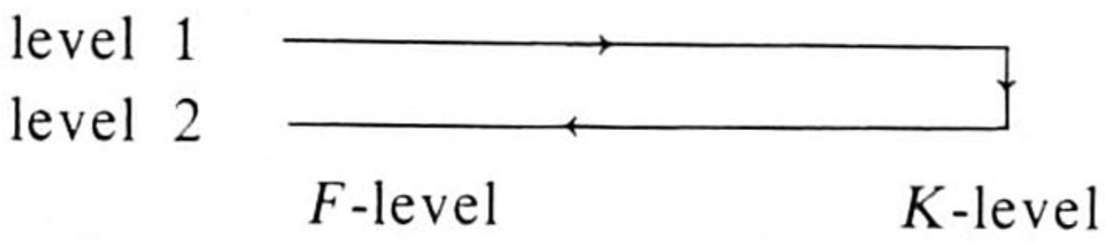
(2*) if $a \neq 0$ and $b \neq 0$ then $P = f_2(V, T, a, b) =$

$$= \frac{V}{V-b}\left(\frac{RT}{V}\right) - \frac{a}{V^2} = \frac{V}{V-b} f_1(V, T) - \frac{a}{V^2}$$

The levels 1 and 2 should not be interpreted directly as the phenomenological and the kinetic level, respectively. Without doubt, (1) was considered as a "first approximation" on the F-level. However, there seems no evidence that (2) was also discovered on this level as a "better approximation". Nevertheless, it is clear, *first*, that this could have been so, *second*, that this would have been without an interpretation of the individual constants a and b, and, *third*, that this might have directed research into looking for an interpretation of them.

As a matter of historical fact, (2) was first discovered theoretically by van der Waals (1873), i.e. on the K-level, by looking for better approximation (than (1)) and starting with ideas about the possible influence of mutual attraction and the volume of the molecules. For this reason it is tempting to call level 1 the phenomenological level, and level 2 the kinetic level. But, formally, they can be distinguished, and history could have been otherwise.

In a scheme we put it as follows:



where the path of arrows indicates actual history.

From the foregoing we may conclude that the direct transition from F-1 to F-2 may be seen as a logically possible step from an idealization to an uninterpreted concretization on the basis of, and only on the basis of, empirical evidence: an *empirical concretization.* On the other hand, the historical path might be called a *theoretical concretization.* The argument underlying the latter will have our main interest not only for historical, but also for systematic reasons. Textbooks on physics including a chapter on the kinetic theory need an argument for the transition which should be required to be essentially correct and understandable by the student.

Textbooks generally agree upon an elementary "kinetic derivation" of the ideal gas law (1). Neglecting molecule-volume, mutual attraction, *and wall-attraction*, it is argued that the pressure P is the mean momentum exchange by the (perfect) collisions of the molecules with the wall.

This leads to

$$(3) \qquad P = \frac{2}{3} n\bar{u}$$

where n indicates the (number-) density of molecules (i.e. the number of molecules per volume-unit) and u the mean kinetic energy of the molecules. In the first approximation we have also

$$(4) \qquad n = \frac{N}{V}$$

where N is Avogadro's number, i.e. the number of molecules in a mole.

Using the reduction postulate

$$(5) \qquad \bar{u} = \frac{3}{2} kT$$

where $k = R/N$, i.e. Boltzmann's constant, we get (1) from (3) and (4).[2]

For the theoretical transition from (1) to (2) there are roughly three different accounts, to be called the naive, the standard and the sophisticated account.

The naive account

The naive account (going back to van der Waals (1873)) starts by reconsidering (1), not (3), but it uses "molecular" arguments. It says, *first*, that the molecules, due to their own volume, have only an effective volume $V - b$ at their disposal, where b is proportional to the volume of one molecule. *Second*, due to the mutual attraction of the molecules, one molecule near the wall is attracted by a force proportional to the density and hence to $1/V$; moreover, the number of molecules is also proportional to $1/V$. Hence, the "inner" pressure is increased by a force proportional to $1/V^2$, say a/V^2, where a is some individual gas constant. Combining these two arguments, i.e. substituting in (1) $V - b$ for V and $P + a/V^2$ for P, we get (2), i.e. the law of van der Waals.

Although this account has some plausibility at first sight, it is highly problematic. Because it uses molecular arguments it should be possible to treat them as leading to corrections in the derivation of (3), and then, using (5), it should bring us to (2). Unfortunately, there does not seems to be a way to integrate the correction arguments, in the present formulation, in the derivation of (3).

The standard account

The "standard" argument (e.g. Blinder (1969), Borghouts (1976), Sommerfeld (1952)) is very elegant in this respect. It starts from (3) by noting that, given the elementary argument leading to (3), n should be interpreted as the density of molecules *near the wall* n_w, to be distinguished from the inner density n_i. Only the latter may be equated (approximately) with N/V. Hence, (4) turns into

$$(6) \qquad n_i = \frac{N}{V}$$

and (3) should be replaced by

$$(7) \qquad P = \frac{2}{3} n_w \bar{u}$$

The correction arguments, which will be sketched in a moment, now lead to what might be called a concretization of the idealization assumption

$$(8) \qquad n_w = n_i$$

leading from (7), using (5) and (6), to (1).

The resulting concretization (of course, still an approximation) is

$$(9) \qquad n_w = \frac{V}{V-b} n_i - \frac{aN}{V^2 RT}$$

Substitution of (9) in (7), using (5) and (6), leads now to (2), i.e. the law of van der Waals.

The two sub-arguments (going back to Sauter (1949)) are roughly as follows.

Volume. Within the gas the disposable volume per volume-unit for each molecule can be argued to be, in the first approximation, proportional to $1 - 8n_i v$, where v is the volume of one molecule. Near the wall, however, the disposable volume is proportional to $1 - 4n_w v$. Supposing now that the density is proportional to the disposable volume we get the equation

$$(10) \qquad \frac{n_w}{n_i} = \frac{1 - 4n_w v}{1 - 8n_i v}$$

which leads, together with (6) and putting $b = 4Nv$, to

$$(11) \qquad n_w = \frac{V}{V-b} n_i$$

Attraction. Because of density differences the mutual attraction of the molecules will lead to a potential energy of the molecules near the wall E_w, which will be proportional to the density. Hence, roughly we may put $E_w = \varepsilon \frac{N}{V}$; we will also put $a = N^2\varepsilon$. According to the famous Boltzmann

argument for the effect of potential differences on density, we get in the present case

$$(12) \qquad n_w = n_i\, e^{-E_w/kT} = n_i\, e^{-\frac{\varepsilon N}{VkT}} = n_i\, e^{-a/VRT}$$

which leads, in a first approximation, to

$$(13) \qquad n_w = n_i - \frac{aN}{V^2RT}$$

Combining the two corrections (11) and (13), and omitting second-order corrections, we get (9) as promised. Note, by the way, that these corrections are such that the volume of the molecules has an increasing effect on the density near the wall, whereas the mutual attraction has a decreasing effect.

Thus far the standard account seems to be a perfect illustration of the general claim: the corrections are integrated in the argument leading to (3) which brought us to (7).

However, we have not so far taken into consideration the attraction of the molecules by the wall, i.e. *wall-attraction*. At first sight this might not seem to matter. Teytbooks usually include one or other argument to the effect that, although the wall-attraction will be considerable, e.g. compared with the mutual attraction, it does not effect the validity of (3). That is, e.g. if we assume a potential energy arising from the wall-attraction, we can nevertheless derive (3). All this is allright, but it becomes clear from such a "no-influence argument" that "n" in (3) should now be interpreted as the inner density n_i. This destroys the standard account, which started by interpreting "n" as n_w (i.e. from (3) to (7)), on the basis of the elementary argument leading to (3) neglecting wall-attraction. Hence, the student is left with the problem how to combine the standard-corrections and the "no--influence" argument for wall-attraction. Fortunately for the student, textbooks based on the standard account are usually composed, consciously or unconsciously, in such a way that he or she will not even discover the problem: the relevant sections are relatively far away from each other.

The sophisticated account

Now we will sketch a sophisticated account which lacks the defect of the standard account. Two appendices will go into some detail.

Let us add that although there is no sharp distinction between the kinetic theory and (classical) statistical mechanics, our account certainly still belongs to the kinetic theory. In textbooks on statistical mechanics one can also find sophisticated derivations of the law of van der Waals, by suitable approximations of the so-called second virial coefficient. But these expositions are based on the fundamental statistical principles of statistical mechanics. The important point of our account is that it is already possible to have a non-defective derivation within the kinetic theory.

There will be two steps in our exposition. *First*, the sophisticated derivation of the ideal gas law. *Second*, the sophisticated derivation of the law van der Waals.

The first step is essentially known in the literature. However, as already said, textbooks prefer a derivation neglecting wall-attraction as the initial step, arguing separately that wall-attraction makes no difference to the result. We have already seen that one objection to this procedure is that it prevents the derivation of the law of van der Waals. A second, no less important, objection is that the neglect of wall-attraction is only realistic in the sense that it does not influence the result. It is highly unrealistic in the sense of the actual state of affairs of gas in a container. In fact there is a fluent transition from an attractive to a repulsive force field due to the wall. In Nowak's terms one might say that wall-attraction and wall-repulsion are both principal factors for the pressure in the ontological sense. That the neglect of wall-attraction does not influence the result is merely a matter of mathematical coincidence, and not of approximation.

The main lines of the first step are as follows. The kinetic theory considers an equilibrium state of an isolated amount of gas as a statistically stable state, i.e. as a continuous sequence of momentary states for which the following *local* quantities are constant in time: the local density of molecules, and the local mean kinetic energy in all directions. Now it is possible to show that such a stable state is only possible, in view of the mutual interactions and the interactions with the wall, if these interactions are elastic and if, in addition, the following invariance conditions are satisfied: the local mean kinetic energy is the same in all directions (isotropy), and the local total mean kinetic energy is the same everywhere (homogeneity).

On the basis of these assumptions it now follows that there are unique global quantities: $\bar{u}$, the global total mean kinetic energy, and p, the kinetic pressure, i.e. the resultant force per surface-unit exerted by the molecules on the wall. The latter value is of course going to be identified with the "phenomenological" pressure P, the former is related with absolute temperature T, according to the standard relation $\bar{u} = (3/2)\,kT$.

For the rest of the argument leading to the ideal gas law we refer to *Appendix* 1. Here it suffices to state the crucial idealizing assumption occurring in it. Due to the wall-attraction/repulsion the density near the wall will not be constant. From this there results a net effect of the mutual interactive (repulsive and attractive) which causes *additional* changes in the density near the wall. It is these additional changes of density which are not taken into account.

The second step, leading to the law of van der Waals, takes these additional changes into account, of course, by making some assumptions

about the mutual interactive forces. We refer to *Appendix* 2, from which it will also become clear that it is really a correction in (a concretization of) the argument in *Appendix* 1. *App.* 2 concludes by deriving and justifying the current interpretations of the constants a and b, roughly an attraction-factor and a volume-(repulsion) factor, respectively.

As far as we know, the argument in *Appendix* 2, which remains within the kinetic theory, is not known in the literature. We hope to have argued convincingly that it should be used instead of the standard account in advanced textbooks on the kinetic theory. Te be able to use it, one is also forced (as is the present author) to include the argument of *Appendix* 1. The advantage of this would be that the magical treatment of wall-attraction in current textbooks (it has no influence on the result, *hence* we may neglect it in the argument) would disappear.

Appendix 1: *Sophisticated derivation of the ideal gas law.*

Basic assumptions

As the *global* quantities of an equilibrium state we have introduced in the main text the volume V, the (global) mean kinetic energy $\bar{u}$ and the kinetic pressure p.

To introduce the relevant individual and local quantities we need the subset X of those space-points in Euclidean space reachable by the molecules. We assume a coordinate-system with directions $i = 1, 2, 3$.

As *individual* quantities we have, besides the position of a molecule, its (time-invariant) mass m, its velocity $v = (v_1, v_2, v_3)$ and its kinetic energy $u = (u_1, u_2, u_3)$ which are related in the following way

$$(1) \qquad u_i =_{df} \tfrac{1}{2} m v_i^2, \; u =_{df} \tfrac{1}{2} m v^2,$$

such that, because of

$$(2) \qquad v^2 = v_1^2 + v_2^2 + v_3^2,$$

we get

$$(3) \qquad u = u_1 + u_2 + u_3.$$

The basic *local* quantities are defined as mean values in a region around $\mathbf{x} \in X$: $n(\mathbf{x})$, the number-density of molecules around $\mathbf{x}$; $\overline{v^2}(\mathbf{x})$ $(\overline{v_i^2}(\mathbf{x}))$, the local mean square velocity around $\mathbf{x}$ (in the i-direction); and $\bar{u}(\mathbf{x})$ $(\overline{u_i}(\mathbf{x}))$, the local mean kinetic energy around $\mathbf{x}$ (in the i-direction). These local quantities are assumed to be constant in time (diachronic assumptions), which presupposes that they are related to appropriate volume-elements.

It is easy to check that, because of (2) and (3),

$$(4) \qquad \overline{v^2}(\mathbf{x}) = \overline{v_1^2}(\mathbf{x}) + \overline{v_2^2}(\mathbf{x}) + \overline{v_3^2}(\mathbf{x})$$

$$(5) \qquad \bar{u}(\mathbf{x}) = \overline{u_1}(\mathbf{x}) + \overline{u_2}(\mathbf{x}) + \overline{u_3}(\mathbf{x}).$$

The two basic synchronic assumptions of kinetic theory for an equilibrium state are

I $\quad \overline{u_1}(\mathbf{x}) = \overline{u_2}(\mathbf{x}) = \overline{u_3}(\mathbf{x}) = (1/3)\,\overline{u}\,(\mathbf{x})$ (isotropy)

II $\quad \overline{u}\,(\mathbf{x}) = \overline{u}$ (homogeneity)

The assumption that we are considering an amount of *pure* gas implies

III all molecules have the same mass.

Using III, I and II can be reduced to resp.

I′ $\quad \overline{v_1^2}(\mathbf{x}) = \overline{v_2^2}(\mathbf{x}) = \overline{v_3^2}(\mathbf{x})$ (and therefore, $= (1/3)\,\overline{v^2}(\mathbf{x}) = (2/3)\,\overline{u}\,(\mathbf{x})/m$)

II′ $\quad \overline{v^2}(\mathbf{x}) = \overline{v^2}(= 2\overline{u}/m)$

where $\overline{v^2}$ is the global mean square velocity.

In order to get recognisable formulas we will occasionally use the (standard) reduction relation $\overline{u} = (3/2)\,kT$, but it would be possible to use it only at the end. The trivial, but necessary, reduction relation $P = p$ will only be introduced at the end.

Thermal pressure

We define the *local thermal pressure* $q_i(\mathbf{x})$ at $\mathbf{x}$ *in the i-direction* as the mean momentum-exchange pro time-unit and pro surface-unit, around $\mathbf{x}$, perpendicular to the i-direction. By a well-known argument, that is, the argument normally used to calculate the kinetic pressure on the wall directly (and neglecting wall-attraction), we get, without any particular assumption, except III:

(6) $\quad q_i(\mathbf{x}) = n\,(\mathbf{x})\,m\overline{v_i^2}(\mathbf{x})$

Using I′ we get from (6)

(7) $\quad q_1(\mathbf{x}) = q_2(\mathbf{x}) = q_3(\mathbf{x}) = (1/3)\,n\,(\mathbf{x})\,m\overline{v^2}(\mathbf{x}) =_{df} q\,(\mathbf{x})$

i.e. the local thermal pressure at one place $\mathbf{x}$ is equal in all directions, hence we may write simply $q\,(\mathbf{x})$.

Using II′ we get from (7)

(8) $\quad q\,(\mathbf{x}) = (2/3)\,n\,(\mathbf{x})\,\overline{u} = n\,(\mathbf{x})\,kT$

Potential energy (the Boltzmann argument)

If the molecules are subject to a conservative force field (i.e. depending only on position and not on time, nor velocity) then there is a differentiable function $E\,(\mathbf{x})$, the *local potential energy*, such that $-dE\,(\mathbf{x})/d\,(x_i)$ is the force acting in the i-direction an a molecule with position $\mathbf{x}$. Now the assumption that a column of gas needs to be in dynamical equilibrium leads, without further restriction, to the differential equation

$$(9) \qquad q\,(\mathbf{x}+\Delta\mathbf{x}) = q\,(\mathbf{x}) - n\,(\mathbf{x})\,\frac{dE\,(\mathbf{x})}{dx_i}\,\Delta x_i \qquad \text{if } \Delta x_j = 0 \text{ for } j \neq i$$

for which the solution is easily found to be

(10) $n(\mathbf{x}')/n(\mathbf{x}) = exp(-E(\mathbf{x}')/kT)/exp(-E(\mathbf{x})/kT)$

with special case

(11) $n(\mathbf{x}') = n(\mathbf{x})\, exp(-E(\mathbf{x}')/kT)$ if $E(\mathbf{x}) = 0$.

Kinetic pressure

Assuming that the wall gives rise to a conservative force field for the molecules we obtain as a general expression for the kinetic pressure, which is by definition the resultant force per surface-unit exerted by the molecules on the wall:

$$(12) \qquad p = \int_0^{\infty} n(x)\left(-\frac{dW(x)}{dx}\right)dx = -\int_0^{\infty} n(x)\, dW(x),$$

where

— the positive x-axis is chosen to be the coordinate perpendicular to the wall inside the gas, such that we may assume $n(x) = 0$ for $x \leqslant 0$,

— $W(x)$ is the potential energy of a molecule at distance x due to the adhesive and repulsive forces of the wall,

— the minus-sign for the application of "action is minus reaction" has disappeared in order to count p positive in the "inside-outside-direction".

For the following argument the only assumptions about $W(x)$ we need are that it is differentiable, that it is constant far from the wall, and hence that it may be chosen to be 0 there, and, finally that it increases asymptotically as x approaches 0. In sum:

(13) $dW(x)/dx$ exists; if $x \to \infty, 0$ then $W(x) \to 0, \infty$ respectively.

Of course, (13) leaves room for the realistic assumption that as x goes from 0 to ∞, the force $-dW(x)/dx$ decreases from infinitely repulsive (positive) to adhesive (negative), reaches a minimum and then increases to approach 0.

From (11) we know that $n(x)$ will not be constant near the wall and hence there will be some net result of the mutual interactions of the molecules: the interaction potential energy $I(x)$, due to mutual cohesive and repulsive forces will be locally different. However, we are interested in states with increasing volume and hence with decreasing density and therefore with decreasing differences in interaction potential, i.e. we may assume

(14) if $V \to \infty$ then $I(x) - I(\infty) \to 0$ for all x

and hence we may apply (11) simply to $W(x)$, which transforms (12) into

$$(15) \qquad \text{if } V \to \infty \text{ then } p \to n(\infty)\, kT \int_0^{\infty} d\left(exp\left(-W(x)/kT\right)\right)$$

and, using (13), we get

(16) if $V \to \infty$ then $p \to n(\infty)\, kT$ $(= q(\infty))$.

Of course, besides (14), we have also for *one mole* of gas

(17) if $V \to \infty$ then $n(\infty) \to N/V$

From (16) and (17) we get finally, using $P = p$,

(18) if $V \to \infty$ *then* $PV \to NkT = RT$

If we neglect the asymptotic character of (18), it transforms into the ideal gas law.

Note that we would have obtained $(2/3)\, N\bar{u}$, instead of RT, in (18) if we would not have used the reduction postulate $\bar{u} = (3/2)\, kT$. The latter would then have been suggested by the thus revised form of (18).

Appendix 2: Sophisticated derivation of the law of van der Waals

The generality of the argument will become clear by the presentation in three levels of decreasing generality.

In Appendix 1 we have derived (10), i.e. for one coordinate:

(1) $n(x')/n(x) = exp\left(-E(x')/kT\right)/exp\left(-E(x)/kT\right)$

where $n(x)$ is the local density and $E(x)$ the local potential energy. As general expression fo the kinetic pressure we had (12), i.e.

(2) $$p = -\int_0^\infty n(x)\, dW(x)$$

where $W(x)$ is the potential energy due to the wall, for which we assumed the minimal conditions (13):

(3) for $x \in (0, \infty)$ $dW(x)/dx$ exists; if $x \to \infty, 0$ then $W(x)$ $\to 0, \infty$ respectively.

In the final argument in *Appendix 1* we neglected in the application of (2) the local interaction potential $I(x)$, due to the mutual cohesive and repulsive forces between the molecules as soon as the density is not uniform, e.g. near the wall.

Density

Our first assumption concerning the interaction potential is that it is proportional to the density $n(x)$:

(4) $I(x) = Cn(x)$

where C may still depend on individual and global quantities.

Note that (4) implies that the (mean) interaction force is proportional to the derivative $dn(x)/dx$, which is certainly the relevant variable, to say the least in support of (4).

For convenience we put $I(\infty) = I$ and $n(\infty) = n$.

In terms of the total local potential energy

$$(5) \qquad E(x) = W(x) + I(x)$$

we are able to transform (2) into

$$(6) \qquad p = -\int_0^\infty n(x)\, dE(x) + \int_0^\infty n(x)\, dI(x)$$

For the second term in (6) it is easy to derive with (4), using $n(0) = 0$,

$$(7) \qquad \int_0^\infty n(x)\, dI(x) = Cn^2/2$$

For the first term in (6) we use a first approximation of $n(x)$. If we add to the assumption $W(\infty) = 0$ the additional assumption $I(\infty) = 0$ we get from (1) and (5)

$$(8) \qquad n(x) = n\, exp\left(-E(x)/kT\right)$$

From (8) we can directly infer

$$(9) \qquad dn(x) = (-n/kT)\, exp\left(-E(x)/kT\right) dE(x) = \left(-n(x)/kT\right) dE(x)$$

Hence we get as a first approximation of the first term of (6)

$$(10) \qquad -\int_0^\infty n(x)\, dE(x) \approx kT \int_0^\infty dn(x) = nkT$$

Substitution of (7) and (10) in (6) leads to

$$(11) \qquad p \approx nkT + Cn^2/2$$

Temperature

Our next assumption concerning $I(x)$ is that the proportionality constant C is a linear function of T: we put

$$(12) \qquad C = BkT - A$$

This assumption is more ad hoc than (4), but it is also more liberal. Substitution of (12) in (11) leads, after some algebra, to

$$(13) \qquad p \approx nkT(1 + Bn/2) - An^2/2$$

Using $n \approx N/V$ and putting

$$(14) \qquad a = AN^2/2, \; b = BN/2$$

we get from (13)

$$(15) \qquad \left(p + \frac{a}{V^2}\right) \approx \frac{NkT}{V}\left(1 + \frac{b}{V}\right)$$

which may be transformed, if $V \gg b$, into the usual form of the law of van der Waals

$$(16) \qquad \left(p + \frac{a}{V^2}\right)(V - b) \approx NkT \; (= RT).$$

Interpretation of the constants

Combining (4) and (12) we see to have used

$$(17) \qquad I(x) = Bn(x)\,kT - An(x)$$

Our final problem is to justify (17) and to specify interpretations for A and B. We start by making the usual first approximation assumption in statistical mechanics that the interaction between two molecules at distance r is governed by the so-called squate-well potential:

$$(18) \qquad i(r) = \begin{cases} \infty & \text{for } r < 2r_v \\ -e & \text{for } 2r_v < r < 2r_a \\ 0 & \text{for } 2r_a < r \end{cases}$$

where r_v indicates the (volume-) radius of a molecule and r_a the attraction-radius.

In view of (18) it is justified to split $I(x)$ into two parts: I_R, the repulsion potential and I_A, the attraction potential, i.e.

$$(19) \qquad I(x) = I_R(x) + I_A(x)$$

It is easy to approximate $I_A(x)$ on the basis of (18)

$$(20) \qquad I_A(x) \approx \int_{2r_v}^{2r_a} n(x)(-e)\,4\pi r^2 dr = -n(x)\,e\,(8v_a - 8v_m)$$

where v_m indicates the volume of a molecule and v_a the volume of its attraction-sphere.

Combination of (14), (17), (19) and (20) leads directly to the standard first approximation of (A and) a on the basis of (18):

$$(21) \qquad A = e\,(8v_a - 8v_m) \quad \text{and} \quad a = N^2 e\,(4v_a - 4v_m)$$

The remaining question is how to approximate the repulsion potential $I_R(x)$. Because of the infinite value of $i(r)$ for $r < 2r_v$ according to (18) it is not possible to do so in a direct way. We will indicate an informal and a more sophisticated indirect way, respectively.

How does the potential energy due to repulsion arise? The following "history" is quite unrealistic but conceptually elucidating. Suppose one point-molecule is expanding from radius 0 to radius r_v in an environment of molecules with radius r_v and thermal pressure $n(x)\,kT$. This is comparable to the expansion of our molecule to radius $2r_v$ in an environment of point-molecules and thermal pressure $n(x)\,kT$. The work done by the environment can now be expressed by

$$\int_0^{2r_v} n(x)\,kT\,4\pi r^2 dr = n(x)\,kT\,8v_m$$

This work is stored in the molecule, i.e. it is the acquired repulsion potential:

(22) $\quad I_R(x) = n(x)\, kT 8 v_m$

Combination of (14), (17), (19) and (22) leads to the standard aproximation of (B and) b on the basis of (18)

(23) $\quad B = 8 v_m \quad$ and $\quad b = 4 N v_m$

A more sophisticated derivation of (22), and hence (23), can be obtained as follows. For an arbirary point $\mathbf{x}$, $I_R(\mathbf{x})$ is by definition such that the time-average force $\vec{F}(x)$ excerted on a molecule by the collisions of the other molecules can be expressed as

(24) $\quad \vec{F}(x) = -\text{grad}\ I_R(x)$

Where the density $n(\mathbf{x})$ is uniform this net force is zero, but where $n(\mathbf{x})$ is not uniform there will be a net force into the direction of lower density.

$\vec{F}(\mathbf{x})$ can be approximated as follows. Realizing that, according to (18), the centers of two molecules cannot come closer than $2r_v$, $\vec{F}(\mathbf{x})$ can be seen as the result of the thermal pressure $n(\mathbf{x}+\mathbf{r})\, kT$ at each point $\mathbf{x}+\mathbf{r}$ on the surface of the sphere with radius $2r_v$ (i.e. $|\mathbf{r}| = 2r_v$) and concentric with a particular molecule which is supposed to be fixed at $\mathbf{x}$. For a small part dS of this surface around $\mathbf{x}+\mathbf{r}$ the resulting force is $d\vec{F} = n(\mathbf{x}+\mathbf{r}) kT \vec{u}\, dS$, where $\vec{u}$ is the outward directed unit vector.

For the total force $F(\mathbf{x})$ we get in this way

(25) $\quad -kT \int\limits_{|\mathbf{r}| = 2r_v} n(\mathbf{x}+\mathbf{r})\, \vec{u}\, dS$

According to a standard integral theorem of Gauss, (25) is equivalent to

(26) $\quad -kT \int\limits_{|\mathbf{r}| \leqslant 2r_v} grad\ n(\mathbf{x}+\mathbf{r})\, dV$

where dV stands for a small part of volume.

We get an approximation of (26) by replacing grad $n(\mathbf{x}+\mathbf{r})$ by its approximate mean value grad $n(\mathbf{x})$ and using $\int dV = 8 v_m$. In this way (26) reduces to

(27) $\quad -kT 8 v_m\ grad\ n(\mathbf{x}) = -\text{grad}\,(n(\mathbf{x})\, kT 8 v_m) \approx \vec{F}(\mathbf{x})$

Combining (27) and (24) and restricting to the coordinate x we get (22), and hence (23).

Reasoning backwards we may conclude from (19), (20) and (22) that

(28) $\quad I(x) = 8 v_m\, n(x)\, kT - e\,(8 v_a - 8 v_m)\, n(x)$

can be justified as approximation of the interaction potential energy, on the basis of (18), and that it can be used succesfully to derive, again by some approximations, the law of van der Waals, even in such a way that the constants retain their standard approximation, on the basis of (18), in statistical mechanics.

Of course, the chosen set-up of the argument is such that the first step can be used to try out more sophisticated approximations of $I(x)$ than (12): fulfilment of (4), i.e. proportionality with $n(x)$, is the only requirement to obtain (11) as approximation of the central integral (2).

The argument here presented may not only be used in advanced textbooks on the kinetic theory, as a better alternative to the standard argument criticised in the main text. It may also be used to make explicit the local interaction potential (28), of which we may conclude that it is implicitly contained in the current derivations of the law of van der Waals in statistical mechanics based on the square-well potential (18).

NOTES:

* This is an enlarged version of a lecture held on November 27, 1981 at the University of Poznań. I was very much stimulated during my research by discussions with Henk Zandvoort and also by some correspondence with A.N. Borghouts. My fellowship at the Netherlands Institute for Advanced Study in 1982/1983 gave me the opportunity to write the final version. I am also grateful to Anne Simpson from the NIAS for improving the English and to Wolfgang Balzer for pressing me to rethink my initial interpretation of the findings. Finally, I am grateful to K. Bärwinkel and H.J. Schmidt who suggested some improvements in *Appendix 2*. The responsibility for the way in which I used their suggestions is, of course, mine.

[1] At several places (e.g. (1980), p. 29) Nowak suggests that the "higher level function" can be constructed as a function of the "lower level function" and a function of the secondary factors. In the present case this would come about to: $f_2(V, T, a, b) = g(f_1(V, T), h(a, b))$. However, it is clear from (2*) that this cannot be done. What we can do, and implicitly did in (2*), is writing $f_2(V, T, a, b) = g(f_1(V, T), V, T, a, b)$. Although it is trivial, it is in many cases illuminating, as for instance in (2*). That the function g in (2*) does not depend on T is clearly coincidental.

[2] In fact the reduction postulate (5) is much stronger than necessary. In another paper (1982), we have argued in general that reduction of phenomenological to kinetic thermostatics can be based on the reduction postulate which identifies thermal equivibrium with having equal mean kinetic energy. This weaker principle has two advantages. It prevents "reduction" in the other direction (note that (5) allows the derivation of (3) from (1)).Moreover, it can really be seen as a pure ontological identification.

BIBLIOGRAPHY:

S.M. Blinder (1969), *Advanced Physical Chemistry*, Macmillan, London

A.N. Borghouts (1976), *Warmteller en Kinetische gastheorie*, Delft UP, 4

Theo A.F. Kuipers (1982), "The Reduction of Phenomenological to Kinetic Thermostatics", *Philosophy of Science*, 1, 107–119

Leszek Nowak (1976), "On Some Interpretation of the Marxist Methodology", *Zeitschrift für allgemeine Wissenschaftstheorie*, 1, 141–183

— (1980), *The Structure of Idealization. Towards the Systematic Interpretation of the Marxian Idea of Science*, Synthese Library, Reidel, Dordrecht/Boston/London

Fritz Sauter (1949), "Über die Zustandsgleichung verdünnter realer Gase", *Annalen der Physik*, 6, 59–66

A. Sommerfeld (1952), *Thermodynamik und Statistik*

J.D. van der Waals (1873), *Over de continuiteit van den gas- en vloeistoftoestand*, Leiden